Working Group on Complex Materials

Chair: Ward Plummer, University of Tennessee

Facilitator: Zhi-xun Shen, Stanford University

Working-group members: Massimo Altarelli, European Synchrotron Radiation Facility (France); Thomas Callcott, University of Tennessee Knoxville; C.T. Chen, Synchrotron Radiation Research Center (Taiwan); Jun-Liang Chen, Synchrotron Radiation Research Center (Taiwan); Jonathan Denlinger, University of Michigan; Makoto Doi, Lawrence Berkeley National Laboratory; Wolfgang Eberhardt, Forschungszentrum Jülich; David Ederer, Tulane University; Kwang Yong Eun, Korea Institute of Science & Technology; Atsushi Fujimori, University of Tokyo, Japan; Eric Gullikson, Lawrence Berkeley National Laboratory; Michael Hochstrasser, Pennsylvania State University; Craig Horne, Lawrence Berkeley National Laboratory; Zahid Hussain, Lawrence Berkeley National Laboratory; Scott Kellar, Lawrence Berkeley National Laboratory; Miles Klein, University of Illinois Urbana-Campaign; Guy Lelay, CNRS Université de Provence (France); Hong-Ji Lin, Synchrotron Radiation Research Center (Taiwan); Ingolf Lindau, Stanford Synchrotron Radiation Laboratory; Martin Magnuson, Uppsala University (Sweden); Giorgio Margaritondo, IPA-EPFL (Lausanne, Switzerland); Nils Mårtensson, University of Lund (Sweden); Maurizio Matteucci, National Research Council (Italy); Joseph Nordgren, Uppsala University (Sweden); Se-Jung Oh, Pohang Light Source (Korea); Joe Orenstein, University of California Berkeley; Fulvio Parmigiani, Catholic University; Jim Patel, Lawrence Berkeley National Laboratory; Rupert Perera, Lawrence Berkeley National Laboratory; Phil Platzman, Lucent Technologies; Art Robinson, Lawrence Berkeley National Laboratory; George Sawatzky, University of Groningen (Netherlands); John Spence, Arizona State University; Yasuhisa Tezuka, Lawrence Berkeley National Laboratory; Ku-Ding Tsuei, Synchrotron Radiation Research Center; Xingjiang Zhou, Lawrence Berkeley National Laboratory.

1. Introduction

Materials research provides the foundation on which the economic well being of our high-tech society rests. The impact of advanced materials (alloys, ceramics, composites, lasers and other optical media, liquid crystals and other "soft matter," polymers, magnetic alloys and compounds, semiconductors, superconductors, etc.) ranges dramatically over every aspect of our modern world from the minutiae of daily life to the grand scale of our national economy. Invariably, however, breakthroughs to new technology trace their origin both to fundamental research in the basic properties of condensed matter and to applied research aimed at manipulating properties (structural, physical, chemical, electrical, magnetic,

optical, etc.) by controlling the structure (both electronic and geometric), often in ways that do not otherwise occur in nature. Figure 1 is a beautiful illustration of "tunable" materials properties [1]. In this "switchable" mirror, the concentration of hydrogen incorporated into yttrium by varying the hydrogen pressure determines the reflectivity. The top figure is for the yttrium film before hydrogenation, where the material is metallic and acts like a mirror. At the bottom is the transparent non-metallic phase (YH_3).

Indeed, nearly every materials-research program, large or small, has as its ultimate objective the design of a material with novel or at least predictable properties. Such materials engineering requires learning how to fabricate materials with the desired composition and structure over length scales down to the level of individual atoms. According to the dictionary, engineering means "the application of scientific and mathematical principles to practical ends..." Materials research is about developing the scientific and mathematical principles.

To take a few examples from the recent past:

- The fabrication technology that makes the ultraminiaturized integrated circuit (the most famous case of an artificial structure) a reality derives both from the unique properties of silicon and the research that taught materials scientists how to harness them.
- The next generation of high-density magnetic storage devices will read information with magnetic sensors derived from research on multiple ultrathin layers (superlattices).
- Optical communications is partially the result of research that increased the transparency of glass in optical fibers by a factor of 10,000 since 1965.
- Research into artificially layered semiconductors has led to the semiconductor lasers used in compact-disk players and CD-ROM drives.

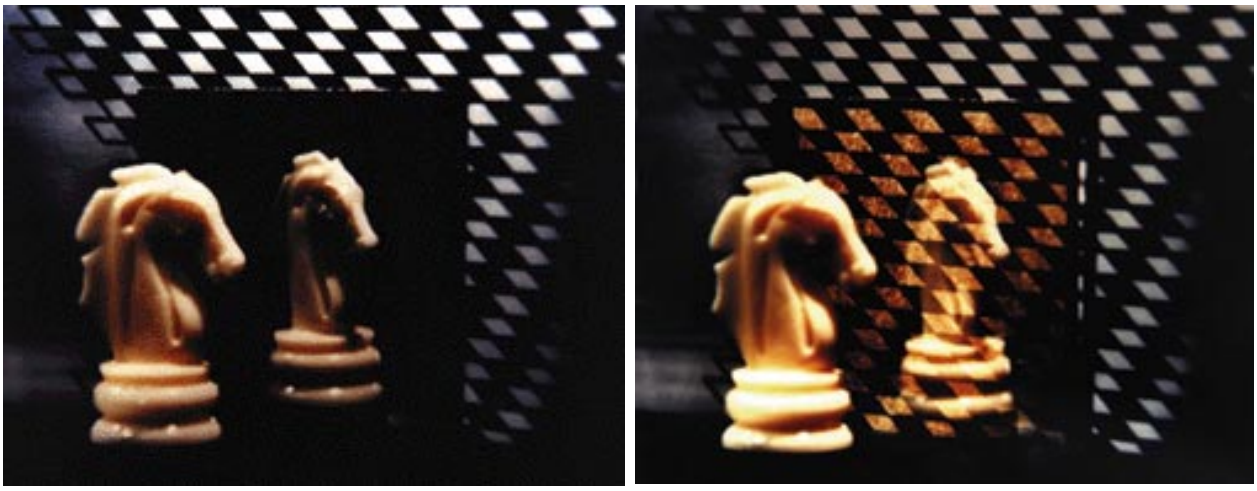

Figure 1. These photographs show the behavior of a 500-nm-thick yttrium film covered with 20-nm palladium protection layer. The film and the transparent chess-board pattern behind it are illuminated from behind to monitor the frequency dependence of the transmitted light and from in front to see the mirror image of the white knight that is placed just in front of the film. The illumination is the same for the two photographs. The yttrium film, the chess-board pattern, and the knight are placed within a glass tube of 20-cm diameter that can be evacuated and filled with hydrogen gas at a pressure of up to 105 Pa. The left figure is for the yttrium film before hydrogenation, where the material is metallic and acts like a mirror. The right figure is in the trihydride γ phase and has become highly transparent, so you can see the chess board illuminated from the back. [Figure taken from reference 1.]

- The development of corrosion-resistant body parts stems from research in ion implantation of metals.
- The newest skis, tennis rackets, and bicycles are made from composite materials that resulted from research into the structure-function relationship.
- Those winking, blinking lights in the tennis shoes our children wear are piezoelectric devices with roots in research on ceramics.

Truly, as a recent report from the American Physical Society attests, "Materials research is a key to our quality of life and our competitiveness in global markets" [2].

New materials and new technologies will continue to change our lives in the future. Clues to where future breakthroughs are expected may be gleaned from a list of what might be called the five "hot topics" among the solid-state part of the condensed-matter community. Undoubtedly, such a list is "fashionable" and subjective, but it is still enlightening. Our selection of the hottest topics includes.

- Non-conventional *superconductivity* (including that in materials with high critical temperatures; that is high-T_c materials).
- *Magnetism* in multielectron extended systems.
- *Reduced (or confined) dimensionality* in mesoscopic systems, nanostructures, quantum wells, etc.
- *Beyond the single-particle picture* in a general description of correlated systems and in transport in synthetic materials (the quasiparticle model does not work in these systems).
- *Novel Phase Transitions*.

Increasingly, the frontiers of materials research include what we are calling "complex materials," as reflected in our list of hot topics, which is dominated by phenomena occurring in this very broad class of materials. In the following sections, we review the features of complex materials, summarize the experimental tools needed to characterize them, and recommend specific capabilities required at the Advanced Light Source (ALS) in order to be at the forefront of research in this field.

It should be noted that the future development of complex materials depends on sophisticated materials synthesis, characterization, and theoretical understanding all working hand in hand. The ALS with its unique capabilities in spectroscopy and spectromicroscopy of local electronic structure should be a major player in this process, with a primary role in the characterization of the electronic and magnetic structure of these materials. *The important point is that the electronic structure of materials is accessible primarily in the vacuum ultraviolet (VUV) and soft x-ray spectral region for which the ALS is optimized, and it is the electrons that determine the properties of a material.*

2. Complex Materials

We use the term "complex materials" to describe materials characterized by strong coupling between the electronic, spin, and structural degrees of freedom. Most of the examples discussed in the following sections are transition-metal oxides, but the class of complex materials is actually much broader; for example, it includes rare-earth compounds, organic metals, superconductors, and the recently discovered organic magnetic conductors. Interest in complex materials stems from the richness of their physical properties and the matching complexity of the underlying physics. Figure 2 shows the phase diagram of the perovskite $La_{1-x}Ca_xMnO_3$ [3], which displays an abundance of physical properties, magnetic transitions, metal-to-nonmetal transitions, colossal magnetoresistance (CMR), charge

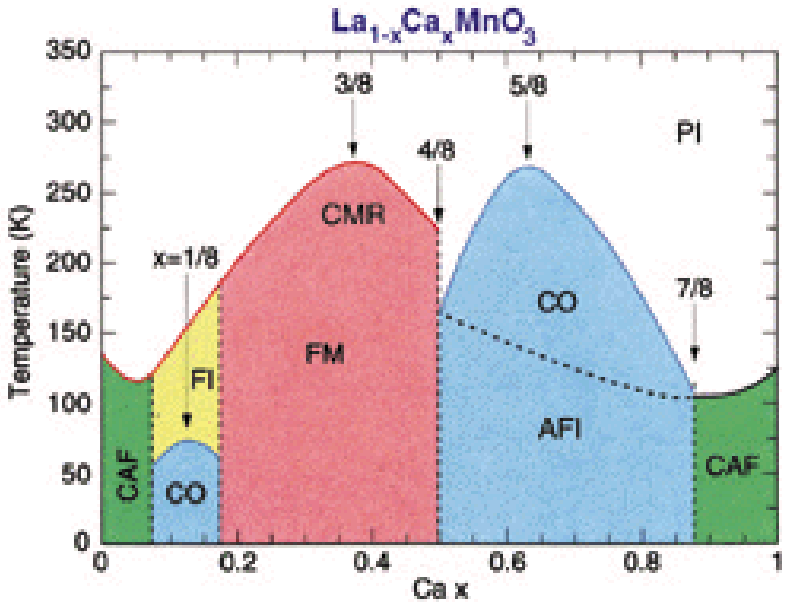

Figure 2: The phase diagram of $La_{1-x}Ca_xMnO_3$, which shows an abundance of physical properties, such as ferromagnetism (F), antiferromagnetism (AF), paramagnetism (P), canted antiferromagnetism (CAF), colossal magnetoresistance (CMR), charge ordering (CO), as well as metal-to-nonmetal transitions (M to I), etc. [Figure taken from reference 3.]

ordering, etc. The strong coupling between the electronic, spin, and structural degrees of freedom is at the heart of the novel behavior of these materials, as well as the resulting technologically important applications.

Tunability of properties is a significant attraction of complex materials that derives directly from their complexity, which thus becomes an asset rather than an obstacle. In contrast to the artificially engineered materials, such as integrated circuits, nature's aid can be enlisted in engineering complex materials. This is often referred to as "the complexity paradigm." For example, many of these materials have two sublattices. In the case of the high-T_c materials, one is a charge reservoir and the other is the electronic backbone. For the CMR materials, one lattice provides the electron backbone and the other hosts the localized magnetic system. However, owing to the strong coupling between degrees of freedom, there is as yet limited fundamental understanding at the atomic level of complex materials to guide attempts at engineering them.

2.1 Novel Features and the Scientific Issues

We have compiled a list of interesting physical phenomena observed in complex materials, so that we have a framework upon which our recommendations for the ALS can be compared. The feature numbers will be referenced in subsequent sections.

1. What Is the Role of Electron Localization in the Exotic Properties of Complex Materials?

Manifestations of localization include Mott insulators and Mott transitions in transition-metal oxides, Anderson localization, and Mott-Anderson transitions in disordered systems, and heavy Fermions in f-electron systems. The rare-earth and actinide intermetallics exhibit the broadest

dynamic range from simple metals to the exotic phenomena that are of current intense theoretical and experimental interest. These include the Kondo effect, spin fluctuations, exotic forms of superconductivity, Kondo insulators, and non-Fermi-liquid behavior.

2. Can We Find and Characterize Quantum Phase Transitions (Low-Temperature Phase Transitions from One Quantum State to Another)?

One example would be the transition from a Mott insulator to a Fermi-liquid state. Another would be the transition from an antiferromagnetic insulator to a d-wave superconductor.

3. Is Phase Separation a General Characteristic of Strongly Correlated Metal-Oxide Systems?

Frustration seems to be a general property of the doped transition-metal oxides such that spatially invariant solutions may not be appropriate to the ground state. Rather, a spontaneous separation into two or more phases may be more accurate. The length scales should be accessible to resonant soft x-ray scattering probes of charge and spin order and dynamics. Examples are found in the nickelates, manganites, and cuprates and have been predicted theoretically using strongly correlated electronic models.

4. What Is the Nature of the Quasiparticle States near the Fermi Energy?

What is the nature of these states; how do transition-metal and non-metal (oxygen) orbitals participate? What is the spin-wave behavior in antiferromagnetic (AFM) and ferromagnetic (FM) phases? Can we understand the fluctuations (commensurate or incommensurate) in the AFM materials?

5. How Does the Superconducting State in the Cuprate High-Temperature Superconductors Arise from a Highly Incoherent Normal State?

Single-particle spectroscopies (e.g., angle-resolved photoemission and tunneling) see not a robust quasiparticle above T_c but mostly incoherence. This is also the case with two-particle spectroscopies, such as optical response and Raman scattering. The superconducting state is quite like a Bardeen-Cooper-Schrieffer (BCS) state with evidence of coherent superconducting quasiparticles in the one- and two-particle spectroscopies. How does this come about?

6. What Are the Novel Features of Superconductors with Nodes in their Order Parameters: Non-Conventional Superconductivity.

The order parameter (OP) is believed to be d-wave in cuprates and some organic superconductors and p-wave in ruthenates and heavy-Fermion superconductors. Among the new phenomena that should be revealed is breaking of time-reversal symmetry at interfaces and other places where the dominant OP is suppressed.

7. What Is the Interplay among Spin, Charge, and Orbital Ordering in Transition-Metal Oxides?

These orderings produce dramatic changes in physical properties, such as resistivity and magnetoresistance, and can be tuned by small changes in composition and by application of a magnetic field. How and why do these superlattices form and what is the relation between the different orderings, including phase separation?

8. What Are the Elementary Excitations of Systems that Undergo Coupled Spin and Orbital Order?

Some metal-oxide systems order their spins and orbital moments in a coordinated manner. Since the energy scales of the spin wave, orbital waves, and the coupling between them are all comparable, the elementary excitations will also be of mixed character. Soft x rays are ideal for probing these excitations because of their ability to couple directly to the orbital moments.

9. What Are the Roles of (Local) Phonons, Orbital Ordering, and Phase Separation in Colossal-Magnetoresistive (CMR) Materials?

In the CMR materials the carriers interact so strongly with local orbital (L), spin (S), and lattice (u) excitations that their transport is strongly affected. It is believed that a combined L/S/u field moves with the carrier or perhaps localizes the carrier or a group of carriers. At issue is the proper description of the ground state of this field and its excitations. Because of their element specificity and strong spin-orbit sensitivity, the soft-x ray spectroscopies are ideal for studying the static order and the excitations.

10. What Is the Effect of Symmetry Reduction Caused by an Interface?

At an interface, in the ideal case, the magnetic order (spin and orbital) will obey boundary conditions, as will the other fields that couple to these order parameters, such as the macroscopic strain and sublattice strains. The result is generally one of frustration, with perhaps the local suppression of the dominant order parameter(s) coupled with the existence near the interface of sub-dominant order parameters. At issue is the appropriate description of the order near the interface and of the localized excitations that will exist there. In the case of superconductors with a non-conventional order parameter, a similar situation will obtain.

11. Does Spin-Charge Separation Exist Beyond One Dimension?

In one dimension, theory clearly says that the physical electron separates into spin (S) and charge (Q) parts. This has recently been confirmed by angle-resolved photoemission. Much less clear is the case of higher dimensionality: Is the incoherence in the one-particle property that is a universal property best described as due to S-Q separation or simply to strong coupling effects?

2.2 The Richness of Phenomena in Complex Materials

Before describing our perspective of the potential impact of the ALS on research in complex materials it is useful to give several scientific examples to illustrate the richness of phenomena associated with these materials. Figure 3 shows the dramatic changes in the resistivity of two perovskite manganites ($Nd_{1/2}Sr_{1/2}MnO_3$ and $Pr_{1/2}Sr_{1/2}MnO_3$) [4]. Both systems exhibit metal-to-nonmetal transitions upon cooling and become ferromagnetic below the Curie temperature T_C (see arrows). Below the Néel temperature T_N, both become antiferromagnetic, but the resistance of the $Nd_{1/2}Sr_{1/2}MnO_3$ increases by about four orders of magnitude more than that of the $Pr_{1/2}Sr_{1/2}MnO_3$ compound. The large increase is due to charge ordering in the $Nd_{1/2}Sr_{1/2}MnO_3$ compound.

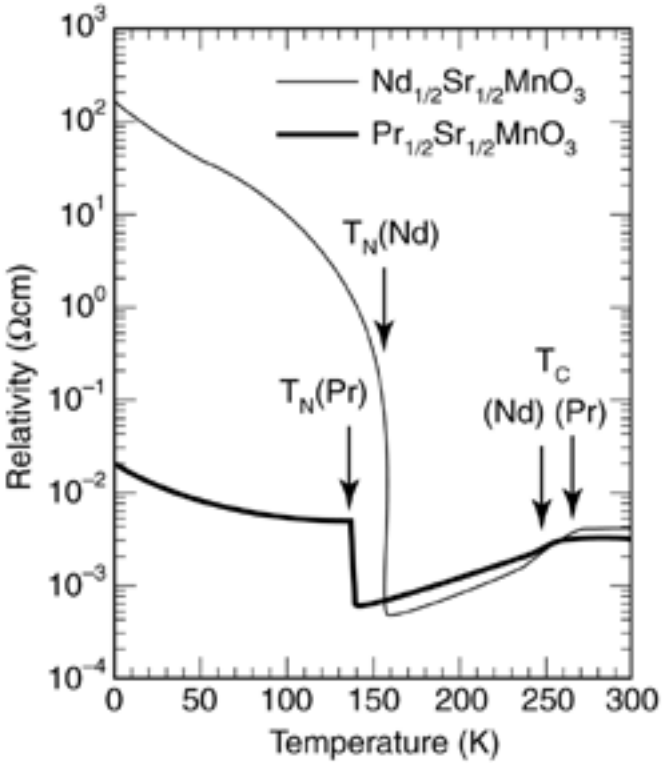

Figure 3. Temperature dependence of the resistivity of $Pr_{1/2}Sr_{1/2}MnO_3$ and $Nd_{1/2}Sr_{1/2}MnO_3$. Thick and thin arrows denote transition temperatures for praseodymium and neodymium manganites, respectively. [Figure taken from reference 4.]

Table 1 presents a few examples from a subset of complex materials—the oxides of 3d transition metals—to illustrate the diversity and tunability of their physical properties. In these materials, the properties are usually tuned by chemical substitution, as is the case with the magnetic anisotropy in the spinel ferrites, the critical temperature in the high-T_c superconductors, the magnetoresistance in the manganites, etc. Of course, even for 3d transition-metal compounds, the oxides are only part of the story. The halides and chalcogenides are as diverse, although much less research has been done on them. Going beyond the 3d transition-metal compounds to what has been referred to as the extended-electron 4d and 5d transition-metal oxides opens new opportunities, as witnessed by the flurry of activity in the ruthenates, which exhibit p-wave superconductivity, bad-metal behavior, and strange magnetic properties.

Table 1. Examples of the diversity (tunability) of physical properties of the 3d transition-metal oxides.

Property	**Materials**
Metals	CrO_2, Fe_3O_4, $La_{1-x}Sr_xCoO_3$, $SrRuO_3$
Insulators	Cr_2O_3, CoO, Fe_2O_3
Magnetic Semiconductor	(Pr, Lu)Ru_2O_7
Metal-Insulator Transition	VO_2, V2O_3, Ti_4O_7, $Cd_2Os_2O_7$
Superconductors	(La, Sr)$_2CuO_4$, $LiTi_2O_4$
d-Wave Superconductors	YBCO, Bi2212
Piezo-Ferroelectric	$BaTiO_3$, CuCl
Catalyst	Fe, Co, Ni Oxides
Ferromagnets	CrO_2, (La, Sr)MnO_3
Antiferromagnets	MnO, NiO
Ferrimagnets	γFe_2O_3, $MnFe_2O_4$
Colossal Magnetoresistance (Spin Electronics)	(La, Ca)MnO_3
Charge Ordered	(La, Sr)$_2NiO_4$

Synchrotron-based spectroscopic measurements have been key in understanding the origin of many of the interesting properties of these materials. For example, over the last decade, high-resolution angle-resolved photoemission spectroscopy from the Stanford Synchrotron Radiation Laboratory (SSRL) and the University of Wisconsin Synchrotron Radiation Center (SRC) using photon energies from 15 eV to 30 eV have made a significant impact on our understanding of high-temperature superconductors and related materials. Examples of this include the detection of d-wave gap structure, the normal state pseudogap in the underdoped samples, and the spin-charge separation in one-dimensional $SrCuO_2$. The last is a clear example of the breakdown of the quasiparticle concept, which is the very foundation of the standard model (Fermi liquid) of metals and superconductors. Figure 4 displays a cartoon illustrating the new concept of spinon and holon in a one-dimensional system. The accompanying data show a comparison of dispersion of a single hole in one-dimensional and two-dimensional cases. In the conventional picture, one expects the one-dimensional dispersion to be only half of that of two-dimensional dispersion, in strong contrast to the data which shows that the one-dimensional dispersion is three times the two-dimensional dispersion. This very puzzling data can be naturally explained by the realization of spin-charge separation in one dimension.

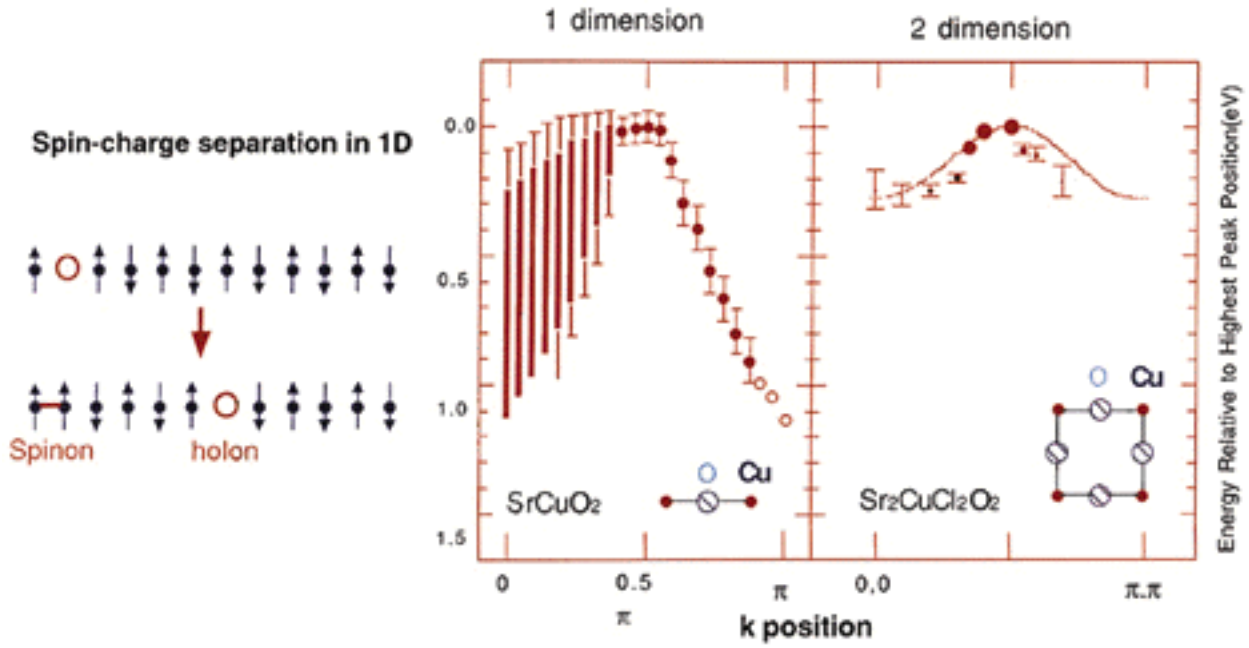

Figure 4. Data from an SSRL experiment that provides the first experimental indication for spin-charge separation in a one-dimensional system. The energy dispersion of a single hole in one-dimensional and two-dimensional cases contrast qualitatively with what one expects from a conventional picture. One expects the one-dimensional dispersion to be only half that of the two-dimensional dispersion. The data show that the one-dimensional dispersion is about three times the two-dimensional dispersion. This very puzzling data can be quantitatively explained by the realization of spin-charge separation in one dimension, as depicted in the cartoon, which illustrates the new concept of spinon and holon in a one-dimensional system. [Figure taken from reference 5.]

Recently, at SSRL a clean experimental example of the breakdown of the quasiparticle concept has been found in two dimensions by a comparison of angle-resolved photoemission spectroscopy (ARPES) data from samples of pure Bi2212 and Bi2212 doped with 0.6% zinc. Doping with 0.6% zinc completely devastated the otherwise sharp "quasiparticle peak" in the pure Bi2212 sample ($T_c \approx 91$K). Similarly dramatic contrast was observed between the spectra in the normal and superconducting states, demonstrating the breakdown of the quasiparticle concept in the normal state.

3. Recommendations

The ALS is a third-generation synchrotron source. Its power lies in the exceptional brightness that it provides in the energy range from about 100 eV to about 1000 eV. As such, it can become a premier facility for the investigation of complex materials. On the other hand, there is nothing truly unique about this facility for most spectroscopy experiments. If you want to do high-resolution angle-resolved photoemission, you can go to SSRL, SRC, or the National Synchrotron Light Source (NSLS). If you want to do spin-polarized photoemission measurements, you schedule time at NSLS, and you go to Europe, if you want soft x-ray emission or absorption data. Users will come to the ALS because it is an easy place to work or because it is an exciting place to work. Neither is true at present.

We believe that the ALS can become an excellent facility for the investigation of important properties of complex materials, but it must be driven by the scientist and the science, not by the machine and the beamlines. People drive good science, so strong outside user groups must be an integral part of any vibrant program at the ALS. With this concept in mind, our recommendations for desired capabilities at the ALS integrate three factors.

- The importance of the specific measurement capability.
- The quality of the "outside scientists" willing to push and support the beamline.
- The "uniqueness" of the measurement capability.

The recommendations are prioritized into two categories. Category I comprises the capabilities that clearly satisfy the two most important factors—participation by excellent outside scientists and importance to the field of complex materials. Category II comprises capabilities that are important to the field, but at present there is not an excellent outside scientist driving the experiments. Our recommendation is clear: Do not proceed with the Category II capabilities until an outside user group with appropriate credentials submits a proposal or until scientific leaders are recruited. In an attempt to give the reader a perspective of the areas of importance of each capability, in the following, the numbers in square brackets refer to the novel phenomena discussed in Section 2.

3.1 Category I: Facilities That Should Be Implemented at the ALS for the Study of Complex Materials

3.1.1 High-Resolution Angle-Resolved Photoemission [3, 5, 6, 11]

For most of the complex materials, angle-resolved photoemission is the only technique capable of measuring the Fermi contour, which is absolutely essential information for understanding the exotic properties of these materials. In addition, this technique can measure energy gaps and properties related to gaps, such as the pairing symmetry, novel order parameters at surfaces and interfaces, pseudogap and pairing correlation in the normal state, and pseudo gap and localization (Coulomb gap and Anderson Transition). Angle-resolved photoemission offers a direct test of the quasiparticle picture of solids, dynamics of charge, spin and orbital degrees of freedom. Quantum phase separation may be observed, as well as spin and charge separation. An ideal facility would be able to perform extremely high-resolution photoemission experiments ($\Delta E < 5$ meV, $\Delta q < 0.02$ Å^{-1}) over a wide photon-energy range (4 eV to 400 eV) and would have the ability to prepare, cleave, and cool samples.

3.1.2 Optical-Conductivity Measurements: Far-Infrared to Optical Frequencies [1, 2, 8]

This is a powerful and versatile technique for discovery of novel features in the low-energy excitation spectra of complex materials, such as metal-to-nonmetal transitions, the magnitude of gaps, and changes in the spectral weight from single-particle-like to highly correlated, as well as identifying optical phonons. The ideal facility would measure the response of the system being studied from the far infrared (about 10 meV) to the near ultraviolet over a wide range of temperature, polarization, magnetic field, and pressure.

3.1.3 Soft X-Ray (Resonant) Absorption, Emission, and Scattering [4, 7, 8]

In contrast to angle-resolved photoemission, soft x-ray absorption, emission, and scattering are bulk, site-specific techniques. These are photon-in/photon-out experiments, so that they look at the bulk and can be used in the presence of high pressure and high magnetic fields. The advantages of these techniques are associated with the site-specific excitation process, the ability to probe deep into the solid, and the soft x-ray wavelength. Specifically, resonant soft x-ray scattering is an excellent probe of the charge and spin order and dynamics, as well as the elementary excitation of systems that undergo coupled spin and orbital ordering. Soft x rays are ideal for probing the excitation of coupled spin and orbital order because of their ability to couple directly to the orbital moments. Finally, because of the elemental specificity and strong spin-orbit sensitivity, soft x rays are ideal for studying the static order and local density of states.

These soft x-ray techniques are high-energy probes of electronic, vibrational, and magnetic properties of materials; however, with sufficiently high resolution, both in energy and momentum transfer, they can yield important information about the low-energy excitations of the system with site specificity. The challenge is to build a facility with excellent energy resolution (< 0.1 eV) over the wide photon-energy range from 50 eV to 1400 eV. The facility should be user-friendly and have sufficient intensity and spatial resolution to satisfy a broad range of user needs. These are truly photon-hungry experiments.

3.2 Category II: Facilities That Should Be Implemented at the ALS If and Only If Distinguished Outside Users Lead the Scientific Activity

3.2.1 Magnetic Circular and Linear Dichroism [1, 7, 8. 10]

The report of the Working Group on Magnetism and Magnetic Materials describes in detail the magnetic circular dichroism (MCD) techniques. A brief discussion is given here of the importance to complex materials. Soft-x-ray MCD (XMCD) can provide important information on complex materials that is either impossible or very difficult to achieve by other experimental means. This information includes (1) element-specific spin and orbital magnetic moments deduced from MCD data and sum-rules; (2) three dimensional element-specific magnetic hysteresis curves measured by MCD absorption and scattering; (3) local magnetic ordering of disorder and dilute systems determined by magnetic EXAFS; and (4) magnetic interlayer coupling and interface magnetic roughness probed by circularly and linearly polarized resonant magnetic x-ray scattering. The unique MCD capability at the ALS should be the combination of the micro-beam and microscopic techniques with the XMCD spectroscopic capabilities mentioned above.

3.2.2 Spin-Polarized Photoemission

The capabilities of this technique are described in the report of the Working Group on Magnetism and Magnetic Materials. Spin-polarized photoemission is the obvious extension of high-resolution angle-resolved photoemission, since in this technique the dispersion of the minority and majority bands near the Fermi energy can be independently measured as a function of the sample composition, magnetic field, and temperature. The limitation at present is the lower energy and momentum resolution imposed by the low collection efficiency.

4. Detailed Description of Capabilities of Different Characterization Techniques

4.1 Angle-Resolved Photoemission and Resonant Photoemission

High-resolution angle-resolved photoemission has emerged as the ideal tool to study many of the important phenomena associated with complex materials because this experimental technique provides detailed electronic structure information that is the key for a microscopic understanding. Past successful examples in these area include the detection of gap anisotropy, a finding that contributed strongly to the current consensus on d-wave pairing in cuprate superconductors, and the detection of spin-charge separation in one-dimensional cuprates. The impacts of these experiments are illustrated by the extensive citation of photoemission papers by others not working on photoemission experiments. Over the last five years, four photoemission papers were ranked among the annual ten-most-cited physics papers identified by the Science Citation Index of the Institute for Scientific Information.

We expect angle-resolved photoemission with high energy and momentum resolution to continue to play a pivotal role to answer the questions raised earlier. In addition to high-T_c superconductors, where the past examples have beautifully shown the capability of ARPES, other material systems, such as manganites, ruthenates, and vanidates, will also be extensively investigated by ARPES. Improved energy and momentum resolution that can be achieved at ALS will make this technique essential to a vibrant program in complex materials at ALS. In particular, the improved momentum resolution that will be achieved at ALS will definitely bring ARPES experiments to a new level. Because of their large unit cell, the complex materials tend to have small Brillouin zones, making high momentum resolution as important as energy resolution. ALS will uniquely be able to allow its users to conduct very-high-resolution experiments at the 4d-to-4f resonance edge, a capability that is very important to study heavy fermion and Kondo systems.

Utilizing a 43-period undulator and a two-dimensional spatial detector, the next-generation high-resolution beamline now under construction at the ALS will have an energy resolution of about 5 meV (or 50 K) and an angular resolution better than 0.5° or 0.017 $Å^{-1}$ at 24-eV photon energy. This facility is not exactly what we described as the ideal facility. It cannot reach the lowest desirable photon energies. Access to these low energies is important because the electron mean free path is long (bulk properties) and the momentum resolution of the analyzer is better. This deficiency could be corrected by using ultraviolet (UV) lasers in conjunction with the synchrotron.

Another related technique that will be important for studying the highly correlated electronic systems is resonant photoemisison (RP) spectroscopy. In the last few years RP has been successfully exploited to obtain important information on the valence-band structure of transition-metal (TM) and rare-earth (RE) compounds. In particular, in the case of Cu^{2+} compounds, RP has been used to identify the correlation satellites resulting from strong Coulomb repulsion between two localized holes in the bands derived from Cu 3d in the final states. The resonant mechanism originates from the interference between the direct photoemission channel and valence-band electron emission promoted by a hole decay (Fano-type interference). The interfering channels give rise to a strong enhancement of the intensity of the open-shell configuration states. Most often RP has been described in an atomic picture, assuming a high degree of localization of the intermediate state, so that in the cuprate case, for example, the two-hole final state is indicated as a $3d_8$ configuration. Furthermore, an unambiguous identification and systematic studies of the Kondo peak heavily relies on the RP technique, because the peak is obscured by intense overlapping spectral features. Recently, the solid-state effects in the resonance mechanism have been addressed, which can be utilized to address the key issues outlined in Section 2.

For RP to address the key physics issues, *high resolution is essential*. Previous RP experiments were performed using relatively poor energy resolution. In other facilities, high-resolution experiments were typically done using normal-incidence monochromators that do not provide photons with sufficiently high energy to reach the core levels of interest. The brightness at ALS makes it much easier to design a higher energy monochromator with high resolution in the energy range desired for RP experiments. As it stands, a tested ALS monochromator can deliver photons in the 100-eV range with better than 5-meV resolution, much better so far than those instruments being implemented elsewhere.

4.2 Optical Conductivity

The impact of the research at the ALS could be greatly enhanced by developing an end station for measurement of optical conductivity. Optical conductivity probes two-particle excitations near the Fermi surface. It is extremely sensitive to quasiparticle lifetimes and structure in the density of states near the Fermi surface. These properties are explored with energy resolution limited only by k_BT. Polarized measurements are powerful probes of highly anisotropic materials. Because the optical conductivity of a sample can be characterized rapidly, materials can be screened for interesting phenomena.

There are many examples of the power of this technique in the literature, many from the Tokura group in Japan. Here we show one beautiful example, the insulator-to-metal transition in strontium-doped $LaVO_3$ [6]. The doping-induced insulator-metal transition and the resulting dramatic change in the electronic structure shows up clearly in the optical spectra displayed in Figure 5. The optical conductivity spectra at room temperature for $La_{1-x}Sr_xVO_3$ displays a dramatic change as x increases.

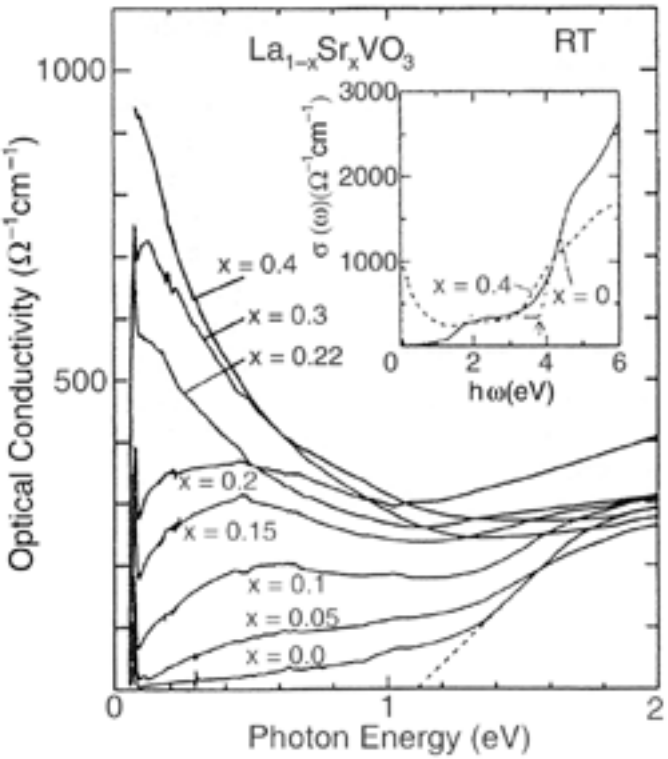

Figure 5. Spectra of optical conductivity at room temperature in $La_{1-x}Sr_xVO_3$. The higher photon energy range was measured at the INS-SOR synchrotron of the Institute for Solid State Physics at the University of Tokyo. [Figure taken from reference 6.]

For x = 0 the parent compound is a Mott insulator with a gap of 1.1 eV (dashed line). Doping with strontium causes the charge-transfer gap to decrease in magnitude until at x = 0.3 the gap closes, as seen in the insert. The low-energy conductivity spectra for the barely metallic samples with x = 0.20 and 0.22 show a non-Drude behavior, implying dominant contribution from the incoherent motion of the charge carriers. In contrast, the spectra for x > 0.3 are Drude-like.

4.3 Soft X-Ray (Resonant) Absorption, Emission, and Scattering

Complex materials, such as high-T_c, colossal-magnetoresistive, and "spin-engineered" magnetic materials containing elements from the 3d, 4d, 4f, and 5d series, have great scientific and technical impact because of the close coupling of their electronic, magnetic, and structural properties. The list of scientific questions presented in Section 2.1 illustrated the nature of the complexity in these materials. Soft x-ray absorption and emission spectroscopies provide a powerful set of tools for sorting out some of the most significant characteristics of those complex systems. Since these are photon-in/photon-out techniques, the materials can be investigated under a wide range of external variables, such as temperature, electric or magnetic field, pressure, etc. Since these spectroscopies involve excitation of core electrons, they are element and site-specific. Selection rules and scattering geometry restrict the angular and crystal momentum. It is also possible to probe electronic and nuclear dynamics on the femtosecond or sub-femtosecond time scale with inelastic x-ray scattering (scanning on and off resonance). Finally, angle-resolved fluorescence studies provide information about bonding geometry and local ordering in both ordered and unordered systems. Standing waves in multilayer structures provide a means to scan across the layers.

Near x-ray thresholds, elastic and inelastic processes that are the x-ray equivalent of electronic resonance Raman processes usually dominate the observed spectra and provide an additional set of capabilities. The scattering intensities depend strongly on localization of intermediate and final states by the introduction of core or valence holes, disorder, or other factors. As a simple example of the use of elastic scattering, diffuse scattering near the specular reflection peak can be used to study the structural disorder in periodic systems, such as multilayers. The additional use of excitation in magnetic multilayers by circularly polarized light from an elliptical undulator could provide the ability to distinguish structural and magnetic disorder at the interfaces in such systems. [Novel feature 10]

4.3.1 Phase Separation

In the doped correlated systems, the long-range magnetic order is usually destroyed at rather small doping levels, as in the high-T_c materials. However there is now a large amount of rather indirect information that the systems have a strong tendency to phase separate into regions of high hole or electron concentrations and insulating magnetic regions. This separation could be dynamic in that the regions can move and can change in shape with time. The same is the case in the colossal magnetoresistance materials which exhibit large regions of ferromagnetic order in an otherwise paramagnetic background above the ferromagnetic-ordering temperature. These regions have dimensions of around 1 nm to 10 nm and may or may not be ordered in space in some way. Hard x rays in general are not very sensitive to valence-electron distributions or valence-charge densities. They therefore are not well suited to study such short-range order. However, at specific resonances, soft x rays are extremely sensitive not only to the valence electron density but also to the local symmetry and even the spin. X-ray scattering in the soft x-ray region at resonance should be developed both to study the above-mentioned structural aspects by elastic scattering, as well as the electronic structure in the inelastic channels. [Novel feature 4]

4.3.2 Orbital Ordering

Transition-metal oxides with partially filled crystal field split levels and subsequent orbital degeneracy exhibit what is now referred to as orbital ordering. It is well known that there is a strong interaction between the orbital ordering and the spin ordering, leading also to speculations of very strong couplings of the spin-wave collective excitations with the collective orbital wavelike excitations. These are of extreme potential importance in the fields of colossal-magnetoresistance materials but also in the materials now proposed for spin electronics in general. Up to now there is little direct information even about the existence of orbital ordering. Since, again, soft x rays are extremely sensitive to the valence-electron charge distribution and the local symmetry, by using resonant x-ray scattering in an elastic-scattering experiment, one can study the nature of this orbital ordering. By looking at the inelastic scattering, one should be able to observe the collective orbital excitations and also the spin-wave excitations. Also, the q dependence can be studied to some extent, but it is limited by the rather long wavelengths usually involved in soft x-ray studies. The strong coupling of the orbital and spin-wave modes can lead to new collective excitations involving bound states of pairs of these excitations and could even lead to new ground states in which these bound states have the lowest energy. Soft x-ray experiments can yield unique information to complement data from scattering experiments with neutrons or hard x rays. [Novel features 7, 8]

4.3.3 Hybridization and Localization

One of the key questions in complex materials is the degree of localization. It has been proposed that the electrons in 4d or 5d transition-metal compounds are "extended," leading to strong hybridizations. An example of the information available from normal fluorescence spectroscopy is provided by spectra from possible the p-wave superconductor Sr_2RuO_4 ($T_c \approx 1.5°K$). In this layered compound, oxygen is present both in layers containing ruthenium and oxygen, and in apical positions lying outside of the ruthenium/oxygen planes. The spectra shown in Figure 6 confirm that hybridization of ruthenium-4d and oxygen-2p

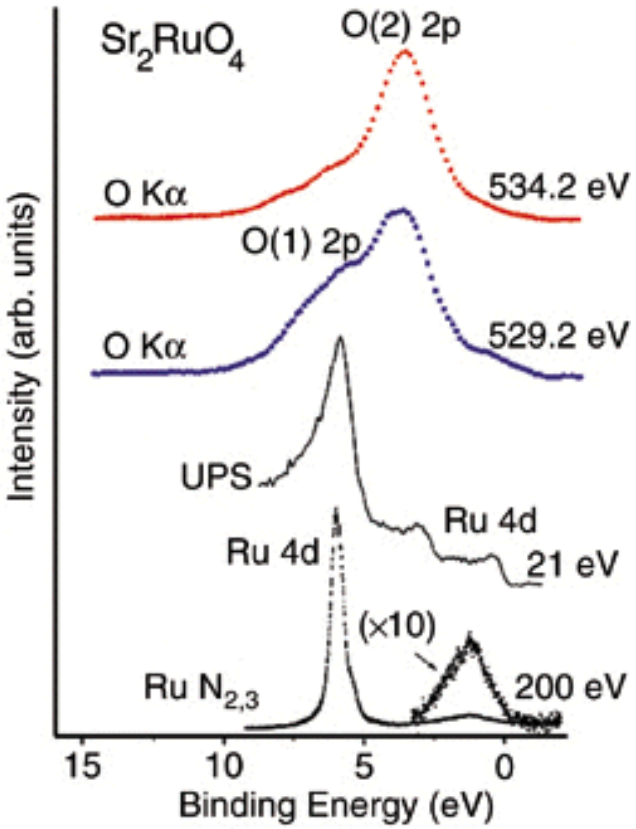

Figure 6. Soft x-ray emission spectra from Sr_2RuO_4. The top two curves show the occupied p density of states for the two different oxygen atoms, O(1) in the ruthenium/oxygen planes and O(2) between the planes. These two states of oxygen are separately excited because the 1s →2p thresholds are different. The ruthenium $N_{2,3}$ spectrum at the bottom provides a measure of the d density of states on the ruthenium. The prominent structure at –6 eV in the O(1) and ruthenium spectra confirms the hybridization of ruthenium-4d and oxygen-2p states predicted by band theory and proves that these are extended electron system. [Figure taken from reference 7.]

states provides the principal bonding for the ruthenium/oxygen plane. The oxygen K spectra provide a measure of the oxygen 2p density of states and the ruthenium $M_{2,3}$ spectra provide a measure of the ruthenium-4d density of states. The spectra from the in-plane and out-of-plane oxygen may be selectively excited by exploiting the chemical shifts of the oxygen 1s core levels. The in-plane oxygen spectra show a strong shoulder with the same binding energy as the ruthenium-4d states, providing strong evidence of hybridization of the oxygen-2p and ruthenium-4d electrons. Figure 6 proves that these 4d transition-metal compounds are indeed "extended-electron" systems, adding a new dimension to research in transition-metal oxides. [Novel feature 1]

4.3.4 d-d Excitations in High-T_c Superconductors

In inelastic scattering, the energy difference between incident and emitted photons is transferred to an electronic excitation. In the transition metal elements, d-d* transitions have particular interest for the study of on-site correlation. In these materials, the energies of the local on-site d-d excitations have been subject to debate as to their possible presence in the mid-infrared spectrum, which is believed to be of importance for high-T_c mechanisms. In a recently reported resonant soft x-ray fluorescence study, insights into these questions were gained by studying the soft x-ray fluorescence (SXF) spectra as a function of excitation energy and angles to gain information about the energies and symmetries of these low energy excitations. The l = 0, 2 selection rules of the two-photon Raman-scattering process make possible the study of dipole-forbidden transitions. The high brightness of the ALS was critical in this experiment because of both the high photon flux and tight focusing required for the experiment. [Novel features 7, 8]

4.3.5 Hydrogen Bonding in Metals—An Application

A very interesting field in materials research concerns the modification of a material's properties by the loading of hydrogen. As illustrated by the photograph in the introduction (Figure 1), it was recently demonstrated that the properties of yttrium metal change drastically when the metal is loaded with hydrogen. It is generally anticipated that there are many other interesting possibilities of tuning material properties in this way. X-ray fluorescence can be used to investigate the electronic properties of these systems under ambient gas pressure or in samples that have been capped to lock the hydrogen in the metal. Figure 7 shows the yttrium-$M_{4,5}$ x-ray fluorescence and absorption spectra of, from the bottom, yttrium metal, yttrium with intermediate loading of hydrogen to form YH_2, and with full loading to form YH_3 [8]. One can clearly see the metallic character of yttrium in the bottom spectrum, i.e., the finite density of states at the intersection of the fluorescence and absorption spectra (Fermi level). For YH_2, hybridization states appear at about 7 eV binding energy and a finite density of states remains at the Fermi level. For the heaviest loading, a 2.5-eV bandgap has opened up, in good agreement with the observation of transparency with a slightly yellowish color of the hydrogenated material. [Novel feature 1]

A facility for soft x-ray absorption, emission, scattering facility at the ALS cannot fully satisfy the specifications listed in Section 3. In the soft x-ray regime, grating monochromators and spectrometers are used and high resolution is achieved by making "big" optical devices. A reasonable sized emission spectrometer (movable) will have a resolving power of ≤2000, providing a resolution of 0.05 eV at 100 eV and 0.5 eV at 1000 eV, which is substantially poorer than can be obtained with either photoemission or visible/UV optical techniques. Given the very low yields of soft x-ray emission and scattering processes which typically require a tradeoff of resolution and intensity, it is unlikely that these measurements could be made at higher resolution even if the capability were theoretically available. Careful thought will have to go into the decision of whether the cost and

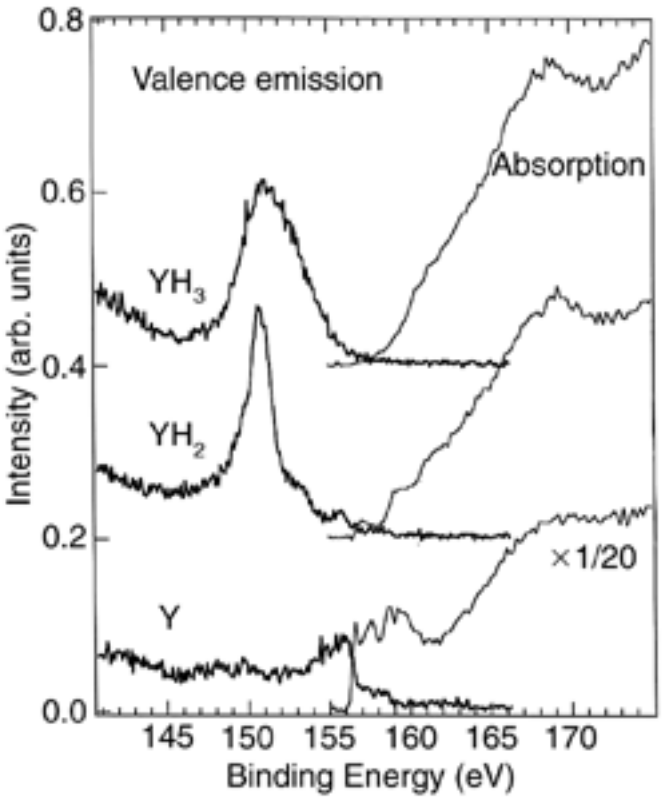

Figure 7. Soft x-ray emission and absorption spectra of Y metal loaded with H to form YH_2 and YH_3 [7]. The emission and absorption spectra show the occupied and empty p-density of states derived from the Y-$M_{4,5}$ spectra. The density of states at the Fermi level in Y and the small but finite density of states in YH_2 are characteristic of metals. For YH_3, a 4-eV bandgap has opened, accounting for the transparency of this material and the "switchable mirror" characteristics shown in Figure 1. [Figure taken from reference 8.]

complexity of a truly high-resolution instrument is justified. It seems certain that a simpler and less expensive movable instrument will make its major contributions by emphasizing such special features as orbital orientation, and element and angular momentum selectivity in normal fluorescence spectroscopy and momentum transfer and $\Delta l = 0$ electronic process in inelastic scattering measurements, leaving the truly high-resolution measurements near the bandgap to other techniques. For example, with a simple optical set up. On the other hand, neither optical measurements or photoemission can provide element or angular momentum selectivity, monitor d-d transitions near the band edges or provide the possibility of resolving sub-femtosecond time scales. To fully understand the electronic properties of complex materials, a full set of spectroscopies will be required with each being used for its particular strengths.

4.4 Magnetic Circular Dichroism

We refer the reader to the discussion of MCD in the report from the Working Group on Magnetism and Magnetic Materials. Here we include a figure showing the performance of an elliptically polarized undulator (Figure 8) for the reason that soft-x-ray MCD can potentially provide important information on complex materials that is either impossible or very difficult to achieve by other experimental means. At

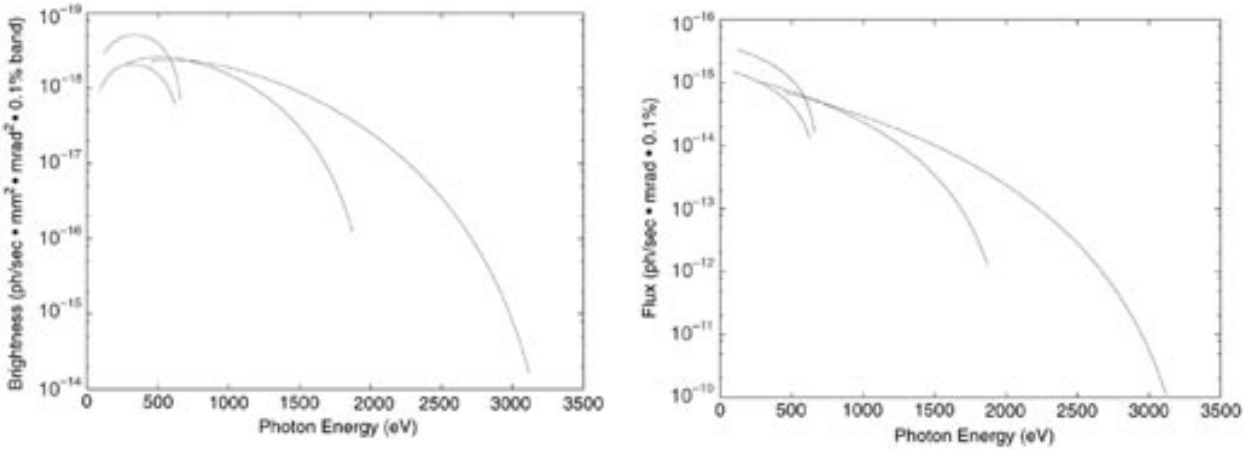

Figure 8. The merit-function brightness and flux for circularly polarized light from the elliptically polarizing undulator (EPU) now under construction at the ALS. The merit-function is the product of the square of the degree of circular polarization and the brightness (or flux). The performance in the fundamental is shown for both circular ($K_x = K_y$) and elliptical ($K_y = 3\ K_x$) modes, where K is the undulator deflection parameter. [Figure courtesy of S. Marks, ALS.]

the workshop, there was considerable debate between the experts in this area concerning the output of an ALS-class synchrotron source, but the curves shown in Figure 8 demonstrate that, in the elliptical polarization mode (using the third and fifth harmonics), useful brightness and flux is available up to 2.5 keV.

4.5 Spin-Polarized Photoemission

This subject is discussed in detail in the report of the Working Group on Magnetism and Magnetic Materials. Here we illustrate one example of the capabilities of this technique and discuss the limitations on energy and resolution. There have been several theoretical predictions that transition-metal compounds could exhibit a half-metallic behavior; that is, one of the spin bands is metallic, while the other is an insulator. This prediction has been confirmed by a group working at NSLS by measuring spin-polarized photoemission from the doped perovskite $La_{0.7}Sr_{0.3}MnO_3$. Figure 9 shows the spin-resolved photoemission spectra taken at 40 K far below the Curie temperature of 350 K [9]. The spectra show that this sample is metallic for the majority spin but insulating for the minority spin, which is exactly what has been predicted theoretically, called a "half-metallic ferromagnet." The authors estimate the insulating gap in the minority bands to be ≈ 0.6 eV and show that the system becomes an insulator above the Curie temperature T_C, as expected.

It is important to understand the inherent limitations in the resolution of this experiment. If we can achieve a resolution of about 5 meV on the best undulator doing angle-resolved photoemission then the loss of at least four orders of magnitude in signal due to a spin-polarized detector will force a decrease in the resolution to keep the same signal. If all of the slits in both the monochromator and analyzer are filled, the required degradation in resolution will be a factor of at least 2 meV to 50 meV. If on the other hand, the brightness of the synchrotron source coupled with good optics creates a situation where neither of the entrance slits are filled, the degradation in resolution for constant signal will be a factor of 100. This experiment is truly photon hungry!

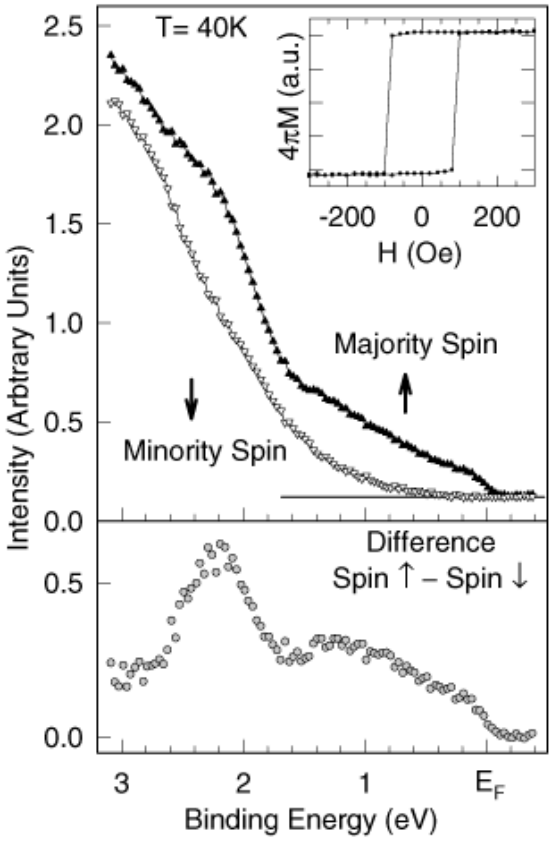

Figure 9. Spin-polarized photoemission spectra of a 1900-Å thick film of $La_{0.7}Sr_{0.3}MnO_3$ taken at T = 40 K ($T_C \approx 350$ K). The photon energy and experimental resolution were 40 eV and 0.2 eV, respectively. A magnetic pulse coil with a magnetic field of about 200 Oe was used for magnetization of the sample. The inset shows the magnetization (M) vs. applied magnetic field (H) hysteresis loop, which was obtained by monitoring manganese L_2-edge absorption of circularly polarized incident light. [Figure taken from reference 9.]

5. References

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